

# BEST AVAILABLE COPY

WO9606132

Publication Title:

Thermoplastic polypropylene blends with mixtures of ethylene/butene and ethylene/octene copolymer elastomers

Abstract:

Thermoplastic olefinic, polymer blends which have superior physical properties and adherence for coating materials such as paints are disclosed. The blends may be formed from various combinations of thermoplastic components such as homopolymers of propylene having an isotactic index which is greater than about 0.93, and/or a crystallinity which is greater than about 56%, and sequentially polymerized blends of polypropylene and ethylene-propylene copolymers, with elastomeric components such as copolymers of ethylene and butene produced with metallocene or Kaminsky catalysts, and copolymers of ethylene and octene produced with metallocene or Kaminsky catalysts. If desired, other components, such as copolymers of ethylene with C3-C15 alpha olefins or fillers, can be included.

-----  
Data supplied from the esp@cenet database - <http://ep.espacenet.com>

**PCT**WORLD INTELLECTUAL PROPERTY  
Organization

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606132A1

(51) International Patent Classification <sup>6</sup> : <b>C08L 23/00, 23/04</b>		<b>A1</b>	(11) International Publication Number: <b>WO 96/06132</b>
			(43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: <b>PCT/US95/10590</b>		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: 21 August 1995 (21.08.95)			
(30) Priority Data: 296,293 25 August 1994 (25.08.94) US 480,175 7 June 1995 (07.06.95) US			
(71) Applicant (for all designated States except US): D & S PLASTICS INTERNATIONAL [US/US]; 1201 Avenue H East, Grand Prairie, TX 75050 (US).		Published With international search report.	
(72) Inventors; and (75) Inventors/Applicants (for US only): SRINIVASAN, Satchit [IN/US]; 1921 Branch Hollow Drive, Carrollton, TX 75007 (US). SZCZEPANIAK, Edward [US/US]; 6911 Hawaii Lane, Arlington, TX 76016 (US). SHAH, Sunit, S. [IN/US]; 318 Santa Fe Trail, Irving, TX 75063 (US). EDGE, David, K. [US/US]; 35659 Huron River Drive, New Boston, MI 48164 (US).			
(74) Agents: FANUCCI, Allan, A. et al.; Pennie & Edmonds, 1155 Avenue of the Americas, New York, NY 10036 (US).			
(54) Title: <b>ENGINEERED OLEFINIC COMPOSITIONS</b>			
(57) Abstract <p>Thermoplastic olefinic, polymer blends which have superior physical properties and adherence for coating materials such as paints are disclosed. The blends may be formed from various combinations of thermoplastic components such as homopolymers of propylene having an isotactic index which is greater than about 0.93, and/or a crystallinity which is greater than about 56 %, and sequentially polymerized blends of polypropylene and ethylene-propylene copolymers, with elastomeric components such as copolymers of ethylene and butene produced with metallocene or Kaminsky catalysts, and copolymers of ethylene and octene produced with metallocene or Kaminsky catalysts. If desired, other components, such as copolymers of ethylene with C<sub>3</sub>-C<sub>15</sub> alpha olefins or fillers, can be included.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**ENGINEERED OLEFINIC COMPOSITIONS****FIELD OF THE INVENTION**

The invention relates to thermoplastic olefinic polymer  
5 compositions and products thereof which have superior  
physical properties including improved wear resistance, as  
well as enhanced adherence for coating materials such as  
paints.

10

**BACKGROUND OF THE INVENTION**

Polymer blends can be formed or shaped into lightweight  
and durable articles such as automobile parts, toys, and  
 housings for various types of equipment. Polymer blends such  
as those with polypropylene and ethylene-propylene  
15 copolymers, however, are difficult to form into products  
which are simultaneously lightweight, easily processed into  
large parts and have surfaces which are durable and adherent  
to paints.

Many attempts have been made to enhance the properties  
20 of products formed of polymer blends such as those formed of  
propylene-ethylene copolymers. Japanese patent publication  
Nos. 57-57049, 62-5460 and 62-5461 each attempt to do so by  
improving the fluidity and stiffness of blends of  
polypropylene with ethylene-propylene copolymer. In  
25 addition, Japanese patent publication No. 61-19651 also  
employs blends which have a large amount of propylene.

The propylene-ethylene copolymer blends shown in the  
above publications suffer from relatively slow  
crystallization rates. As a result, longer cooling periods  
30 are required to manufacture injection molded products. These  
blends, moreover, do not necessarily provide products which  
have excellent durability, such as surface smoothness and  
surface hardness.

Japanese patent publication No. 60-3420 shows a polymer  
35 blend which includes polypropylene, ethylene-propylene  
copolymer, talc and propylene-ethylene block copolymer. This

composition is said to show adhesion for coatings as well as low temperature impact resistance.

Japanese patent Laid-Open publication No. 1-204946 shows a composition comprising ethylene-propylene copolymer, polyethylene, ethylene copolymer, polypropylene and talc. This composition is said to provide products which have dimensional stability.

European patent applications EP 0 519 752 A2 and EP 0496 625 A2 each show blends which comprise ethylene copolymer, propylene polymer and propylene-ethylene "block" copolymer and talc. These blends are said to have good processability for injection molding. Ease of processability is often associated with low melt viscosities (high melt flow rates). These high melt flow rates are often detrimental to other physical properties such as impact strength at low temperatures. Injection molded products formed of these blends are said to have good appearance, low density, good surface hardness and impact resistance, as well as good adhesion.

The above mentioned blends are said to have a morphological structure comprised of crystalline domains embedded in amorphous matrix, contrary to conventional thermoplastic polyolefin blends in which elastomer domains are dispersed in a polypropylene matrix. This structure, however, still has regions where the concentration of elastomers is significantly higher than in surrounding areas, thus effectively exhibiting the existence of elastomeric "macrodomains". These macrodomains have an average size of greater than 4  $\mu\text{m}$ , which may negatively effect certain physical properties of the blend.

Although the compositions shown in the aforementioned references are said to possess good processability, products formed of these compositions tend to be deficient in one or more physical properties such as durability and paint-adhesion. A need therefore continues for thermoplastic blends which can be processed to provide products which have combined properties of superior surface hardness, impact

resistance, processability, flexural modulus, adhesion of coating, and which can be painted using conventional techniques.

5

#### SUMMARY OF THE INVENTION

Thermoplastic compositions formed of olefinic, polymer blends and which have superior physical properties and adherence for coating materials such as paints are disclosed. These blends may be formed from various combinations of thermoplastic and elastomeric components. The thermoplastic component can include a homopolymer of propylene having an isotactic index which is greater than about 0.93 or a crystallinity which is greater than about 56%; a sequentially polymerized blend of a semi-crystalline polypropylene and an ethylene-propylene copolymer; or mixtures thereof. The elastomeric component can include a copolymer of ethylene and a C<sub>3</sub> to C<sub>8</sub> olefin produced with a metallocene or Kaminsky catalyst and having a molecular weight distribution (Mw/Mn) of less than or equal to 3. These catalysts are also called "single site" catalysts.

In this specification, the following definitions will be used to define certain components of these compositions:

Thermoplastic components:

Component (1A): homopolymers and random copolymers of propylene having an isotactic index of greater than about 0.93, preferably greater than about 0.96 or a crystallinity of greater than about 56%, preferably greater than about 65%. These components also have a density of greater than about 0.898 g/cc, preferably greater than about 0.906 g/cc;

Component (1B): a sequentially polymerized blend or "block" copolymer of polypropylene and a copolymer of ethylene with propylene or ethylene with another alpha-olefin; and

Component (1C): a mixture of (1A) and (1B).

**Elastomeric Components:**

As noted above, any copolymer of ethylene and a C<sub>3</sub> to C<sub>8</sub> olefin produced with a metallocene or Kaminsky catalyst and having a molecular weight distribution (Mw/Mn) of less than 5 or equal to 3 is contemplated for use as this component.

Specially preferred components are as follows:

Component (2): copolymers of ethylene and butene ("EB") produced with metallocene, Kaminsky or "single site" catalysts and which have Mw/Mn of less than or equal to 3;

Component (3): copolymers of ethylene and octene produced with metallocene, Kaminsky or "single site" catalysts and having Mw/Mn of less than or equal to 3; and

A mixture of components (2) and (3).

In addition, the present compositions may also include component (4), which is a copolymer of ethylene and a C<sub>3</sub> to C<sub>15</sub> olefin having a crystallinity of at least about 30%.

Copolymers of ethylene with C<sub>4</sub>-C<sub>10</sub> alpha-olefins such as butylene, pentylene, hexylene, septylene, octylene, nonylene, and decylene, are preferred. These olefins and polymers thereof can be branched or linear.

Useful blends of Group (I) include blends of any one or more of thermoplastic components (1A)-(1C) with elastomeric components (2), (3) or mixtures of (2) and (3), such as:

Blend (Ia) formed of combinations of component (1A) with component (2);

Blend (Ib) formed of combinations of component (1A) with component (3);

Blend (Ic) formed of combinations of component (1B) with component (2);

Blend (Id) formed of combinations of component (1B) with component (3);

Blend (Ie) formed of combinations of component (1C) with component (2);

Blend (If) formed of combinations of component (1C) with component (3).

Useful blends of Group (II) include blends of any one of components (1A)-(1C) with component (2) and/or component (3) and/or component (4). Illustrative blends of Group (II) include:

- 5           Blend (IIA) formed of combinations of component (1A) with component (2) and component (3) and EP;  
          Blend (IIB) formed of combinations of component (1A) with component (2) and component (3) and EB;  
          Blend (IIC) formed of combinations of component  
10       (1A) with component (2) and component (3) and component (4);  
          Blend (IID) formed of combinations of component (1B) with component (2) and component (3) and EP;  
          Blend (IIE) formed of combinations of component  
15       (1B) with component (2) and component (3) and EB;  
          Blend (IIF) formed of combinations of component (1B) with component (2) and component (3) and component (4);  
          Blend (IIG) formed of combinations of component  
20       (1C) with component (2) and component (3) and EP;  
          Blend (IIH) formed of combinations of component (1C) with component (2) and component (3) and EB;  
          Blend (IIK) formed of combinations of component (1C) with component (2) and component (3) and component  
25       (4).

Useful blends of Group (III) can be formed of combinations of any of the blends of Groups (I) or (II) with fillers such as talc or calcium carbonate, mica, glass fibers, or other inorganic materials that are conventionally  
30 utilized in the art.

Useful compositions within the scope of the invention can be formed from any of the blends of Groups (I)-(III). These compositions have excellent paintability, a broad range of stiffness values, as well as high impact and tensile  
35 strengths which make them suitable for automotive applications. Blends of any of Groups (I), (II) and (III) also have excellent processability, as exhibited by high melt



flow rates. Thus, the blends of Groups (I)-(III) are particularly suited for injection molding into thin wall articles. Such thin wall articles are used where impact resistance is important. Typical applications include  
5 automotive external parts such as bumpers and bumper covers, as well as interior and exterior automotive component trim.

The blends of the invention can be formed into articles which have a Rockwell R hardness of at least about 60 as measured according to ASTM D-785, a flexural modulus of at  
10 least about 80 kpsi as measured according to ASTM D-790, a melt flow rate of at least about 15 dg/min at 230°C and 2.16 kg as measured according to ASTM D-1238, a minimum density of  $\geq 0.89$  g/cc, and are ductile at about -30°C at a velocity of about 5 mph as measured according to ASTM D-3763. These  
15 articles can be coated with paints such as two-component polyurethanes, acrylics, polyesters, epoxy resins, carboimides, urea resins, and melamine-formaldehyde resins.

Having briefly summarized the invention, the invention will now be described in detail by reference to the following  
20 specification and non-limiting examples. Unless otherwise specified, all percentages are by weight and all temperatures are in degrees Celsius.

#### BRIEF DESCRIPTION OF THE DRAWINGS

25 FIG. 1 is a transmission electron micrograph of the core portion of composition of example No. 5 of the invention.

FIG. 2 is a transmission electron micrographs of the skin layer of the composition of example No. 5 of the invention.

30 FIG. 3 compares injection molding pressures of the compositions of examples 1 and 4 of the invention to commercially available composition.

FIG. 4 compares clamp tonnage to fill a mold with the compositions of examples 1 and 4 of the invention to  
35 commercially available composition D162HF.

FIG. 5 compares the cool/fill times to fill a mold with the compositions of examples 1 and 4 of the invention to commercially available composition D162HF.

## 5 DETAILED DESCRIPTION OF THE INVENTION

Propylene polymers suitable for use in the invention typically have a Melt Flow Rate("MFR") at 230°C and 2.16 kg, when measured in accordance with ASTM D-1238 of about 10 to 80 dg/min, preferably about 35 to 65 dg/min, most preferably  
10 about 45 to 55 dg/min. These MFRs may be attained by controlling polymerization of the propylene monomer, or by addition of an organic peroxide such as a diacyl peroxide or a dialkyl peroxide after polymerization of the propylene is completed. These techniques are well known in the art.

15 The propylene polymer employed may be a propylene homopolymer, or a copolymer of propylene and unsaturated monomers such as maleic anhydride, acrylic acid or trimethoxy vinyl silane. These monomers can be introduced to the propylene by graft copolymerization by methods known in the  
20 art.

Stereospecific catalysts can be employed in well known methods to produce propylene polymers suitable for use as a thermoplastic component according to this invention. Useful stereospecific catalysts can be prepared as disclosed in  
25 Japanese Patent Laid-Open Publication Nos. 56-100806, 56-120712 and 58-104907.

Propylene homopolymers useful as component (1A) have an isotactic index of greater than 0.93, preferably greater than 0.96, and/or a crystallinity greater than 56%, preferably  
30 greater than 65%, as determined from density measurements. These homopolymers are commercially available, and a good example is the series ELTEX P highly isotactic polypropylenes from Solvay.

Crystalline or semi-crystalline polypropylenes can be  
35 employed as component (1A) in the polymer blends of this invention. These may be blended with polyethylenes. Crystalline or semi-crystalline copolymers of propylene and

ethylene also may be used, if desired. When a copolymer of propylene and ethylene is utilized, the copolymer either can be in the form of a random copolymer, a block copolymer, or a graft copolymer.

5       The terminology "crystalline or semi-crystalline" refers to components that are characterized by a sufficient degree of crystallinity, e.g. about 70-100%, such that their behavior is substantially that of a crystalline polyolefin ("crystalline") or by a degree of crystallinity, e.g. about  
10 30-70%, sufficient to cause their behavior to exhibit substantial but not full crystalline polyolefin behavior ("semi-crystalline"). When polypropylene is used as the crystalline or semi-crystalline polyolefin, the polypropylene has 30-98% crystallinity, and typically between 56 and 70%  
15 crystallinity, as determined by X-ray analysis or solvent extraction. The terminology "substantially crystalline" is used to designate those polyolefins having crystallinity of between 30 and 98%.

Ethylene-Propylene ("EP") copolymers which have  
20 differing amounts of ethylene and propylene therein may be employed in component (1B) as well as in the blends of Group (II). EP copolymers for use in the invention can be prepared by copolymerizing ethylene and propylene in the presence of free radical coordination stereospecific polymerization  
25 catalysts, such as Phillips, Kaminsky or Ziegler-Natta catalysts. These preparation techniques are well known.

Generally, EP copolymers useful as component (1B) will be slightly crystalline or substantially amorphous, i.e., greater than 50% amorphous. Preferably, these copolymers  
30 will have a Mooney viscosity of about 10-90 at 100°C. The amount of propylene in the EP copolymer is not particularly limited provided that the Mooney viscosity is within the stated range. The EP copolymers may be completely replaced on a one-to-one basis by terpolymers of ethylene-propylene-  
35 diene monomers ("EPDMs") such as ethylidene norbornene, dicyclopentadiene, 1,4-hexadiene and the like. Useful copolymers may include mixtures of ethylene-propylene and

EPDMs. The total content of ethylene in component (1B) may be between about 0% and about 30%, preferably about 20%. EP copolymers useful in Group (II) blends may have about 30-90% ethylene, preferably about 70% ethylene based on the 5 total weight of the specific blend of Group (II).

The ethylene-butene ("EB") copolymers of component (2) which can be employed in the blends of Groups (I)-(III) are preferably produced by use of metallocene or Kaminsky catalysts. These copolymers typically have a narrow 10 molecular weight distribution, i.e., ( $M_w/M_n$ ) of less than 3, where  $M_w$  = weight average molecular weight and  $M_n$  = number average molecular weight. These EB copolymers can include ethylene in an amount of 5-95%, preferably about 50-90% and more preferably about 80%.

15 The ethylene-octene copolymers of component (3) which can be employed in the blends of Groups (I)-(III) also have a narrow molecular weight distribution ( $M_w/M_n$ ) of less than 3 where  $M_w$  and  $M_n$  are defined as above. These ethylene-octene copolymers can be produced using methods such as those which 20 employ metallocene or Kaminsky catalysts. These ethylene-octene copolymers can have 5-95% ethylene therein, preferably about 50-90% and more preferably about 80%.

Useful blends of Group (I) can include blends of any of (Ia)-(If) as defined above. In blend (Ia), component (1A) 25 can comprise about 50 to 80%, preferably 60 to 70%, remainder component (2); component (1A) can comprise about 50 to 80%, preferably 60 to 70%, of blend (Ib), remainder component (3); component (1B) can comprise about 50 to 80%, preferably 60 to 70%, of blend (Ic), remainder component (2); component (1B) 30 can comprise 50 to 80% of blend (Id), remainder component (3); component (1c) can comprise 50 to 80% of the blend (Ie), remainder component (2); component (1C) can comprise 50 to 80% of blend (If), remainder component (3).

The blends of Group (II) can be formed from combinations 35 of any one of components (1A)-(1C) with components (2) and (3) with component (4). Regarding the latter, it is preferred to use any of EP, EB other than component (2), or

copolymers of ethylene and  $C_3$ - $C_{15}$ , preferably  $C_4$ - $C_{10}$  alpha olefins such as copolymers of ethylene with at least one of propylene, butylene, pentylene, hexylene, septylene, octylene, nonylene, and decylene. Illustrative Group (II)

5 blends include but are not limited to:

about 50 to 80% component (1A) with about 10 to 35% component (2), about 10 to 25% component (3) and about 0 to 20% EP copolymer;

10 about 50 to 80% component (1A) with about 10 to 35% component (2), about 10 to 25% component (3) and about 0 to 20% EB copolymer other than component (2);

15 about 50 to 80% component (1A) with about 10 to 35% component (2), and about 10 to 25% component (3) with about 0 to 20% copolymer of ethylene with at least one of propylene, butylene, pentylene, hexylene, septylene, octylene, nonylene, and decylene;

about 50 to 80% component (1B) with about 10 to 35% component (2), about 10 to 25% component (3) and about 0 to 20% EP copolymer;

20 about 50 to 80% component (1B) with about 10 to 35% component (2), about 10 to 25% component (3) and about 0 to 20% ethylene-butene copolymer other than component (2);

25 about 50 to 80% component (1B) with about 10 to 35% component (2), about 10 to 25% component (3), and about 0 to 20% of a copolymer of ethylene with at least one of propylene, butylene, pentylene, hexylene, septylene, octylene, nonylene, and decylene;

30 about 50 to 80% component (1C) with about 10 to 35% component (2) and about 10 to 25% component (3) with about 0 to 20% EP copolymer;

35 about 50 to 80% component (1C) with about 10 to 35% component (2) and about 10 to 25% component (3) with about 0 to 20% ethylene-butene copolymer other than component (2); and

about 50 to 80% component (1C) with about 10 to 35% component (2) and about 10 to 25% component (3) with

about 0 to 20% copolymer of ethylene with at least one of butylene, pentylene, hexylene, septylene, octylene, nonylene, and decylene.

Each of the ethylene-butene copolymers and ethylene-  
5 octene copolymers of components (2) and (3) respectively, may be slightly crystalline, i.e., have up to about 20% crystallinity as calculated from density measurements. Preferably, each of the ethylene-butene and ethylene-octene copolymers are substantially amorphous. Amorphous ethylene-  
10 butene copolymers are available from Exxon Polymers Co. under the tradename EXXACT. Amorphous ethylene-octene copolymers are available from Dow Chemical Co. under the tradename ENGAGE.

Any of the blends of Groups (I) and (II) optionally may  
15 be combined with fillers such as talc, glass, mica, or calcium carbonate, and the like, preferably talc, to provide blends of Group III. These fillers may be present in an amount of about 0.1 to 10% and preferably about 3-5%.

Each of blends of Groups (I)-(III) provide products with  
20 superior combinations of mechanical and surface properties. Blends of Groups (I)-(III) can be molded into products which show a Rockwell R hardness of at least about 60 as measured according to ASTM D-785, a flexural modulus of at least about 80 kpsi as measured according to ASTM D-790, a melt flow rate  
25 of at least about 10 and preferably about 15 dg/min or more at 230 C and 2.16 kg as measured according to ASTM D-1238, a maximum density of 0.98 g/cc, and are ductile at -30°C at a velocity of about 5 mph as measured according to ASTM D-3763.

Talc usable in the blends of Group III has a particle  
30 size less than 10 microns, preferably less than 5 microns, most preferably about 0.9 micron, and a specific surface area of about 3.5 m<sup>2</sup>/g or more, preferably about 3.5-6.0 m<sup>2</sup>/g. The amount of talc utilized depends on the other component(s) employed in the specific blend of Group (III). Typically,  
35 about 0.1 to 10 parts of talc by weight of the component(s), preferably about 0.1 to 8 parts, and more preferably between about 3 to 5 parts, may be employed.

The talc may be prepared by dry pulverization and subsequent dry classification. The average particle size of the talc employed is a particle size at a cumulative amount of 50% by weight in a cumulative particle size distribution curve obtained by a liquid phase sedimentation light transmission method using, for instance, Model CP manufactured by Shimadzu Corp. The specific surface area measuring apparatus Model SS-100 is produced by Shimadzu Corp.

10 Talc filler employed in the invention need not be treated. However, to improve adhesion between the talc filler and the polymers employed in the blends of Group III, as well as for dispersibility of the talc in those component blends, the talc may be treated with organic titanate  
15 coupling agents, silane coupling agents, fatty acids, metal salts of fatty acids, fatty acid esters, and the like.

Various additives may be combined with any of the blends of Groups (I)-(III) unless they substantially impair the advantageous properties of those component blends. Useful  
20 additives include for example, process stabilizers, antioxidants, ultraviolet absorbers, soaps such as metal soaps, anti-static agents, lubricants, nucleating agents, pigments and dispersant for pigment. In addition, additives capable of imparting higher flexural modulus to the blend  
25 than that imparted by talc can be included. Examples of these additives include fibrous potassium titanate, fibrous magnesium oxalate, fibrous aluminum borate, and carbon fibers.

Morphology of blends of Groups (I)-(III) shows excellent  
30 dispersion of components with the biggest domains being the filler particles. Apart from the filler, the average domain size is less than 2  $\mu\text{m}$ . This indicates excellent compatibility of components as shown in FIGs 1 and 2. This compatibility, combined with the high melt flow rate of the  
35 blend, leads to a characteristic thin layering typically less than about 0.5  $\mu\text{m}$ , near the surface of the injection molded specimens produced from the compositions of the invention.

This is illustrated in FIGs. 3 and 4 which show the morphology of the skin layer of specimens formed from the composition of example 5 of the invention.

The blends of Groups (I)-(III) can be molded or  
5 otherwise formed to produce articles which are lightweight, durable, and have surfaces which are paint receptive. The components also can be pelletized for storage and shipment prior to molding into shaped articles by known methods.

Products formed of any of the blends of Groups (I)-(III)  
10 can be coated with paints, particularly with paints such as commercially available two-component blend polyurethanes to provide products with superior fluid resistance. The blends of Groups (I)-(III) may be coated with paints which have active functional groups such as acrylics, polyesters, epoxy  
15 resins, carboimides, urea resins, melamine-formaldehyde resins, enamines, ketimines, amines, and isocyanates to provide products with improved fluid resistance. These types of paints are well known in the paint and coatings industry.

Products having superior physical properties and  
20 adherence for coating materials such as paints can be prepared by mixing any of the blends of Groups (I)-(III) with, if desired, optional additives by using extruders, Banbury mixers, rollers, brabenders and kneaders. Molded products may be prepared from any of blends of Groups (I)-  
25 (III) by known methods such as injection molding, extrusion molding, and blow molding. Injection molding is preferred.

Blends of Groups (I)-(III) present a significant advantage in injection molding compared to conventional thermoplastic polyolefin blends. A computer simulation of  
30 the molding conditions for the blends of Groups (I)-(III) show lower injection pressure, lower clamp tonnage and shorter cycle time than conventional thermoplastic polyolefin blends having comparable viscosities under standard conditions.

35 The computer simulation, performed using the commercial software package C-Mold from AC Technologies, requires input of rheological and thermodynamic properties of the material



under consideration. These properties can be determined experimentally. The required properties are viscosity as a function of shear rate between  $5 \text{ sec}^{-1}$  and  $10,000 \text{ sec}^{-1}$  at temperatures of  $200^{\circ}\text{C}$ ,  $230^{\circ}\text{C}$  and  $260^{\circ}\text{C}$ ; specific heat as a function of temperature between room temperature and  $250^{\circ}\text{C}$ , as well as density of the material in the solid state and as melted are also required. The thermoplastic polyolefin blend which serves as a control is D162HF. D162HF, available from D&S Plastics, has the highest melt flow rate for commercially available thermoplastic olefin blends.

As shown in FIGs. 5-7, the computer simulation indicates that the maximum injection molding pressure, the clamp tonnage, as well as the fill/cool times for the compositions of Examples 1 and 4 of the invention are much less than for commercially available composition D162HF.

Generally, processing of the components of the invention can be performed using Banbury mixers or twin screw extruders. When a Banbury mixer is employed to prepare any of blends of Groups (I)-(III), a single screw extruder can be used to pelletize that component blend. The resulting pellets then are supplied to an injection molding machine for manufacture of molded articles.

During mixing of the blends of Groups (I)-(III) with a Banbury mixer, the ram pressure in the Banbury mixer is about 30-35 psi. Mixing is continued until fluxing temperature is achieved, i.e., the temperature at which the viscosity of the blend drops sharply. When fluxing temperature is achieved, mixing is terminated and the resulting batch of material is removed from the Banbury mixer. The batch then is ground into chips and/or pelletized in a single screw extruder.

Pellets of the formed component blends are supplied to an injection molding machine for injection molding into shaped products.

### 35 EXAMPLES

The invention will now be explained in more detail with reference to the following examples, which are given merely

to illustrate the invention and are not intended to be limiting thereof.

#### Examples 1-6

5       The compositions of examples 1-6 are given in Table 1. Table 1 also shows the physical properties of the compositions when processed according to the conditions set forth in Table 1A. In Table 1, Ductility Index is measured by using a High Rate Impact Tester machine Model No. RIT-8000  
10 from Rheometrics Company, Piscataway, New Jersey. The RIT-8000 is equipped with a steel probe having a size measuring 0.5" diameter by 12.25" long, and having a weight of about 0.705 lb. The probe has a spherical tip. The probe is accelerated to penetrate a specimen measuring 4" x 6" x 1/8"  
15 at a constant speed of 5 mph. The temperature of the specimen is -30°C.

Ductility Index is calculated from the equation

$$DI = (T - U) / T$$

where

20       DI=Ductility Index,

T represents total energy at the point at which the probe has broken through the specimen, i.e., the point at which the force applied to the specimen by the probe drops to zero, and

25       U represents ultimate energy, i.e., the energy at the point at which the force exerted by the probe on the specimen is at maximum as determined from the force-position curve of force applied by the probe to the specimen vs. the position of the probe. The DI values for each of 3 - 5  
30 specimens are averaged and reported as DI.

Also, in Tables 1 and 2, the peel strength is the force (g/cm) required to peel the paint off substrate, is a measure of adhesive strength of the coating to the substrate.

In determining the peel strength, an injection molded  
35 plaque, formed of a composition of the invention, of size 4x6 inches and 1/8 inch thick, is partially coated with the adhesion promoter RB899 from Morton International Co., and

entirely with a topcoat of R773 from Morton, International Co. to enable lifting the topcoat from that portion of the plaque which is not coated with the adhesion promoter.

Cuts through the topcoat coating are made using a sharp  
5 knife and a metal template to form two or three one cm wide strips. The one cm side strips are slowly peeled from those portions of the plaque which are free of the adhesion promoter. A piece of polyester tape is placed on the peeled off strip to form a "handle" with which the strip is peeled  
10 further.

The prepared plaque is placed into an Instron Tensile Tester (Instron Model 1130).

The force required to peel the strip from the plaque is recorded as a function of the length of peeled off strip  
15 along the plaque. The peeling speed is two inches per minute. The average force in the entire peel is reported as the measure of adhesion strength per one cm of width of peel, i.e., in units of g/cm.

20

25

30

35

TABLE 1

Example No./ Component %	1	2	3	4	5	6	Standard TPO (Control)
PP <sup>1</sup>	62	62	65	65	--	--	--
PP <sup>2</sup>	--	--	--	--	62	--	--
PP <sup>3</sup>	--	--	--	--	--	62	--
EPR <sup>4</sup>	--	--	--	--	--	--	--
EBR <sup>5</sup>	--	--	--	--	--	--	--
Poly(ethylene- co-butene) <sup>6</sup>	22	11	17.5	12	22	22	--
Poly(ethylene- co-octene) <sup>7</sup>	11	22	17.5	23	11	11	--
FILLER <sup>8</sup>	5	5	0	0	5	5	--
HARDNESS <sup>9</sup>	77	69	71	69	75	76	45
FLEXURAL MODULUS <sup>10</sup>	197	190	163	163	214	213	220
MFR <sup>11</sup>	19	22	27	24	18	27	12
DENSITY <sup>12</sup>	.93	.93	.90	.89	.93	.93	1.02
IMPACT @-30C <sup>13</sup>	D	D	D	D	D	D	B
DUCTILITY INDEX	.38	.36	.34	.36	.38	.37	.25
PEEL STRENGTH	1050	1200	780	1200	830	1085	1000

1. Polypropylene, MFR at (230 C, 2.16 kg) = 45 dg/min, ASTM D-1238
2. Polypropylene, MFR at (230 C, 2.16 kg) = 49 dg/min, ASTM D-1238
3. Polypropylene, MFR at (230 C, 2.16 kg) = 56 dg/min, ASTM D-1238
4. Poly(ethylene-co-propylene); C2=50%, C3 = 50%, Mooney Viscosity at 100°C =35
5. Poly(ethylene-co-butene); C2=75%, C4 = 25%; MFR at (190C, 2.16 kg) = 0.8 dg/min
6. EXXACT 4033 from Exxon Co., produced by Kaminsky catalyst process, having C2=80%; MFR at (190 C, 2.16 kg) = 0.3 dg/min, ASTM D-1238
7. C2=80%; MFR at (190 C, 2.16 kg) = 5.0 dg/min, ASTM D-1238
8. Average talc particle size = 0.9 micron
9. Rockwell R hardness measured according to ASTM D-785
10. Kpsi measured according to ASTM D-790
11. dg/min at (230 C, 2.16 kg) as measured according to ASTM D-1238
12. g/cc
13. D=Ductile Failure; B=Brittle Failure measured according to ASTM D-3763

TABLE 1(a)

Processing Conditions						
EXAMPLE/PROCESSING CONDITION	1	2	3	4	5	6
<b>BANBURY MIXING</b>						
ROTOR SPEED (RPM)	185	185	190	190	185	185
RAM PRESSURE (PSI)	32	32	34	34	32	32
TIME TO FLUX (SEC)	95	95	90	90	95	95
FLUX TEMP (°F)	360	360	355	355	360	360
BATCH TEMP (°F)	410	410	410	410	410	410
<b>PELLETIZING SINGLE SCREW EXTRUDER</b>						
END ZONES TEMP (°F)	360	360	360	360	360	360
CENTRAL ZONE TEMP (°F)	380	380	380	380	380	380
SCREW SPEED (RPM)	95	95	95	95	95	95
MELT TEMP (°F)	375	375	375	375	375	375
<b>MOLDING TEMPERATURE</b>						
END ZONE 1	340	340	340	340	340	340
CENTRAL ZONE 2	360	360	360	360	360	360
CENTRAL ZONE 3	360	360	360	360	360	360
END ZONE 4	340	340	340	340	340	340
SCREW SPEED (RPM)	90	90	90	90	90	90
MOLD TEMP (°F)	80	80	80	80	80	80
INJECTION TIME (SEC)	10	10	10	10	10	10
COOLING TIME (SEC)	25	25	25	25	25	25
INJECTION PRESSURE (PSI)	550	550	550	550	550	550
FILLING TIME (PSI)	10	10	10	10	10	10
HOLDING PRESSURE (PSI)	430	430	430	430	430	430
HOLDING TIME (SEC)	15	15	15	15	15	15
BACK PRESSURE (PSI)	50	50	50	50	50	50

Examples 7-11

Table 2 illustrates additional compositions within the scope of the invention. Table 2 also shows the physical properties of the compositions when processed according to the conditions set forth in Table 2a. Ductility index and peel strength are measured as in Examples 1-6.

TABLE 2

EXAMPLE No./ Component (%)	7	8	9	10	11
HIPP <sup>1</sup>	62	62	62	62	62
HIPP <sup>2</sup>	--	--	--	--	--
HIPP <sup>3</sup>	--	--	--	--	--
EPR <sup>4</sup>	33	--	16.5	--	--
EBR <sup>5</sup>	--	33	16.5	--	--
Poly(ethylene-co-butene) <sup>6</sup>	--	--	--	33	--
Poly(ethylene-co-octene) <sup>7</sup>	--	--	--	--	33
FILLER <sup>8</sup>	5	5	5	5	5
HARDNESS <sup>9</sup>	45	60	55	79	74
FLEXURAL MODULUS <sup>10</sup>	175	200	185	203	193
MFR <sup>11</sup>	14	14	14	16	19
DENSITY <sup>12</sup>	0.93	0.93	0.90	0.89	0.93
IMPACT @-30C <sup>13</sup>	D	B	B	B	B
DUCTILITY INDEX	0.37	0.10	0.25	0.28	0.25
PEEL STRENGTH	1100	240	500	450	1180

1. High crystallinity polypropylene, MFR at (230 C, 2.16 kg) = 45 dg/min, ASTM D-1238
2. High crystallinity polypropylene, MFR at (230 C, 2.16 kg) = 49 dg/min, ASTM D-1238
3. High crystallinity polypropylene, MFR at (230 C, 2.16 kg) = 56 dg/min, ASTM D-1238
4. Poly(ethylene-co-propylene); C2=50%, C3 = 50%, Mooney Viscosity at 100°C =35
5. Poly(ethylene-co-butene); C2=75%, C4 = 25%; MFR at 190C, 2.16 kg = 0.8 dg/min, prepared by conventional process, e.g., Flexomer (Union Carbide), Tafmer (Mitsui Petrochemical)
6. EXXACT 4033 from Exxon Co., produced from Kaminsky catalyst, and having C2=80%; MFR at (190 C, 2.16 kg) = 0.3 dg/min, ASTM D-1238
7. C2=80%; MFR at (190 C, 2.16 kg) = 5.0 dg/min, ASTM D-1238
8. Talc, particle size = 0.9 micron
9. Rockwell R hardness measured according to ASTM D-785
10. Kpsi measured according to ASTM D-790
11. dg/min at 230 C and 2.16 kg as measured according to ASTM D-1238
12. g/cc
13. D=Ductile Failure; B=Brittle Failure measured according to ASTM D-3763

TABLE 2 (a)

Processing Conditions					
EXAMPLE/PROCESSING CONDITION	7	8	9	10	11
<b>BANBURY MIXING</b>					
5 ROTOR SPEED (RPM)	185	185	185	185	185
RAM PRESSURE (PSI)	32	32	32	32	32
TIME TO FLUX (SEC)	110	110	110	95	95
FLUX TEMP (°F)	380	380	380	360	360
BATCH TEMP (°F)	420	420	420	410	410
<b>10 PELLETIZING</b>					
END ZONE TEMP (°F)	360	360	360	360	360
CENTRAL ZONE TEMP (°F)	380	380	380	380	380
SCREW SPEED (RPM)	90	90	90	95	95
MELT TEMP (°F)	380	380	380	375	375
<b>MOLDING TEMPERATURE</b>					
<b>15</b> END ZONE 1	360	360	360	340	340
CENTRAL ZONE 2	380	380	380	360	360
CENTRAL ZONE 3	380	380	380	360	360
END ZONE 4	360	360	360	340	340
SCREW SPEED (RPM)	85	85	85	90	90
MOLD TEMP (°F)	80	80	80	80	80
<b>20</b> INJECTION TIME (SEC)	10	10	10	10	10
COOLING TIME (SEC)	25	25	25	25	25
INJECTION PRESSURE (PSI)	750	750	750	550	550
FILLING TIME (SEC)	10	10	10	10	10
HOLDING PRESSURE (PSI)	550	550	550	430	430
<b>25</b> HOLDING TIME (SEC)	15	15	15	15	15
BACK PRESSURE (PSI)	50	50	50	50	50

Examples 12-15

30 Table 3 illustrates additional compositions within the scope of this invention. Table 3 shows the durability of these compositions, as measured by the so-called SLEdge test and high speed cohesive strength test.

35 The SLEdge test utilizes a 15.6 lb pendulum head with a 1" wide painted strip of reaction injection molded polyurethane bolted to it. The pendulum head drops from a 90° position to tangentially impact a 4" x 6" painted

plaque of the molded composition after the plaque has been preheated to 175°F for a minimum of 40 minutes. The extent of the damage is recorded as the area of paint that has been removed from the substrate in square millimeters.

5       The high speed cohesive strength test includes the steps of coating a 4" x 6" x 1/8" injection molded plaque of the composition with 0.1-0.2 mils of a chlorinated polyolefin adhesion promoter and then baking the coated composition for 30 minutes at 80°C. After cooling, a 1.5  
10   cm strip of a 1/16" thick polycarbonate sheet is adhered to the primed surface using a two-component epoxy adhesive. The average force required to cohesively delaminate the sheet from the coated composition is measured in Newtons/meter at 75°F and 180°F.

15       As shown by the tests results, peel area values are in the range of 105-450 mm<sup>2</sup> for conventional compositions while values of 40 mm<sup>2</sup> or less are obtained with the compositions of the invention. When conventional Ziegler-  
20   Natta rubbers are omitted, no peel areas at all occur, as shown by Examples 14 and 15. The inventive compositions also exhibited a significantly greater cohesive strengths than those of conventional compositions.

25

30

35



Table 3

Engineered Thermoplastic Polyolefin Compositions

Components	Comparative Materials								Invention			
	A	B	C	D	E	F	G	H	12	13	14	15
PP homopolymer	49	49	49	49	49	8	37	14	49	49	49	49
PP random copolymer, 3% C2	10	10	10	10	10	0	0	0	10	10	10	10
PP "block" copolymer, 8% C2	0	0	0	0	0	53	25	46	0	0	0	0
EPR1 <sup>ZN</sup>	30	0	0	0	0	28	25	31	20	0	20	0
EPR2 <sup>ZN</sup>	0	30	0	0	0	0	0	0	0	0	0	0
EPR3 <sup>ZN</sup>	0	0	30	0	0	0	0	0	0	0	0	0
EPR4 <sup>ZN</sup>	0	0	0	30	0	0	0	0	0	0	0	0
poly(ethylene-co-butene) <sup>ZN</sup>	0	0	0	0	30	0	0	0	0	0	0	0
poly(ethylene-co-butene) <sup>met</sup>	0	0	0	0	0	0	0	0	10	30	0	0
poly(ethylene-co-octene) <sup>met</sup>	0	0	0	0	0	0	0	0	0	0	10	30
Polyethylene	8	8	8	8	8	8	8	8	8	8	8	8
Talc	3	3	3	3	3	3	3	3	3	3	3	3

Durability	Comparative Materials								Invention			
	A	B	C	D	E	F	G	H	12	13	14	15
SLEdge Test, Peeled area mm <sup>2</sup>	460	425	321	305	105	200	150	400	40	0	20	0
High Speed Cohesive Strength at 75°F, N/m	4000	4100	4100	4600	5200	5000	5500	3800	6200	8000	8200	9000
at 180°F, N/m	1600	1600	1750	1800	1950	1800	2000	1600	2700	3800	3700	4000

Notes

ZN = Ziegler-Natta catalyzed

met = metallocene catalyzed

SLEdge data on all compositions coated with Red-Spot 2k urethane coating  
Cohesive Strength data obtained at a test speed of 200 inches/min

THE CLAIMS

What is claimed is:

1. An automotive component of a molded  
5 thermoplastic article having enhanced wear resistance  
comprising a blend of a thermoplastic component comprising  
component (1A) which is a homopolymer of propylene having  
an isotactic index of greater than about 0.93 or a  
10 crystallinity of greater than about 56%; component (1B),  
which is a sequentially polymerized semi-crystalline blend  
of polypropylene and an ethylene-propylene copolymer; or a  
mixture of component (1A) and (1B); and an elastomeric  
component of a copolymer of ethylene and a C<sub>3</sub> to C<sub>8</sub> olefin  
15 produced with a metallocene or Kaminsky catalyst and  
having a molecular weight distribution (Mw/Mn) of less  
than or equal to 3.

2. The article of claim 1 wherein the elastomeric  
component is component (2), which is a copolymer of  
ethylene and butene; component (3), which is a copolymer  
20 of ethylene and octene; or a mixtures of components (2)  
and (3).

3. The article of claim 1 wherein the blend has a  
melt flow rate of at least about 10 dg/min and wherein the  
thermoplastic component is present in the blend in an  
25 amount of about 50 to 80% and the elastomeric component is  
present in an amount of about 20 to 50%.

4. The article of claim 1 which further comprises  
component (4), which a copolymer of ethylene and a C<sub>3</sub> to C<sub>15</sub>  
olefin having a crystallinity of at least about 30%.

30 5. The article of claim 1 which further comprises a  
filler.

6. The article of claim 1 wherein:  
the Group (I) blends include at least one of:  
blend (Ia) comprising component (1A) with component  
35 (2);  
blend (Ib) comprising component (1A) with component  
(3);

blend (Ic) comprising component (1B) with component (2);

blend (Id) comprising component (1B) with component (3);

5       blend (Ie) comprising component (1C) with component (2); or

blend (If) comprising component (1C) with component (3);

10       and the Group (II) blends include combinations of at least one of:

blend (IIA) comprising combinations of component (1A) with component (2) and component (3) and EP;

blend (IIB) comprising combinations of component (1A) with component (2) and component (3) and EB;

15       blend (IIC) comprising combinations of component (1A) with component (2) and component (3) and component (4);

blend (IID) comprising combinations of component (1B) with component (2) and component (3) and EP;

20       blend (IIE) comprising combinations of component (1B) with component (2) and component (3) and EB;

blend (IIF) comprising combinations of component (1B) with component (2) and component (3) and component (4);

blend (IIG) comprising combinations of component (1C) with component (2) and component (3) and EP;

25       blend (IIH) comprising combinations of component (1C) with component (2) and component (3) and EB; or

blend (IIK) comprising combinations of component (1C) with component (2) and component (3) and component (4).

30       7. The article of claim 1 wherein the propylene polymer in any of components (1A)-(1C) is a polypropylene homopolymer that has a melt flow rate of about 10 to 80 dg/min.

35       8. The article of claim 1 wherein the propylene polymer in any of components (1A)-(1C) is a copolymer of propylene and at least one member selected from the group of maleic anhydride, acrylic acid or trimethoxyvinyl silane.

9. The article of claim 1 wherein the ethylene content of component (1B) or (1C) is about 0-30% based on the total weight of the component.

10. The article of claim 1 wherein the ethylene-propylene copolymers have a Mooney viscosity of about 10-90 at 100°C.

11. The article of claim 10 wherein the ethylene-propylene copolymers of any of components (2)-(3) have about 50-90% ethylene based on the total weight of the component.

12. The article of claim 1 wherein the ethylene-butene copolymers of component (2) or the ethylene-octene copolymers of component (3) are substantially amorphous.

13. The article of claim 4 wherein the alpha olefins of component (4) are have 4-10 carbons.

14. The article of claim 5 wherein the filler is talc or calcium carbonate, glass fibers, mica, or glass microspheres and is present in an amount of about 1-10%.

15. The article of claim 1 wherein the thermoplastic component is present in the blend in an amount of about 40 to 80% and comprises a mixture of components (1A) and (1B), and wherein the elastomeric component comprises a mixture of components (2) and (3) and is present in an amount of about 20 to 60%, wherein component (2) is present in an amount of about 10 to 35% and component (3) is present in an amount of about 10 to 25%.

16. The article of claim 4 wherein the thermoplastic component is present in the blend in an amount of about 50 to 80%, the elastomeric component comprises a mixture of components (2) and (3) is present in an amount of about 20 to 60%, wherein component (2) is present in an amount of about 10 to 35%, and component (3) is present in an amount of about 10 to 25%, component (4) is present in an amount of about 1 to 20%.

17. The article of claim 1 further comprising at least one of stabilizers, antioxidants, ultraviolet absorbers, metal soaps, anti-static agents, lubricants,

nucleators, pigments, fibrous potassium titanate, fibrous magnesium oxalate, fibrous aluminum borate, carbon fibers, and mixtures thereof.

18. The articles of claim 1 further comprising:

- 5       a Rockwell R hardness of at least about 60 as measured according to ASTM D-785,  
      a flexural modulus of at least about 80 kpsi as measured according to ASTM D-790,  
      a melt flow rate of at least about 10 dg/min at 230°C  
10     and 2.16 kg as measured according to ASTM D-1238, and  
      a density of about 0.95 g/cc,  
and wherein the article is ductile at about -30°C when measured according to ASTM D-3763.

19. The article of claim 1 further comprising a  
15     coating of paint thereon, said paint selected from the group of two-component polyurethanes, acrylics, polyesters, epoxy resins, carboimides, urea resins, and melamine-formaldehyde resins.

20. The article of claim 20 in the form of an  
20     bumper, bumper cover, exterior trim part, or interior trim part.

25

30

35

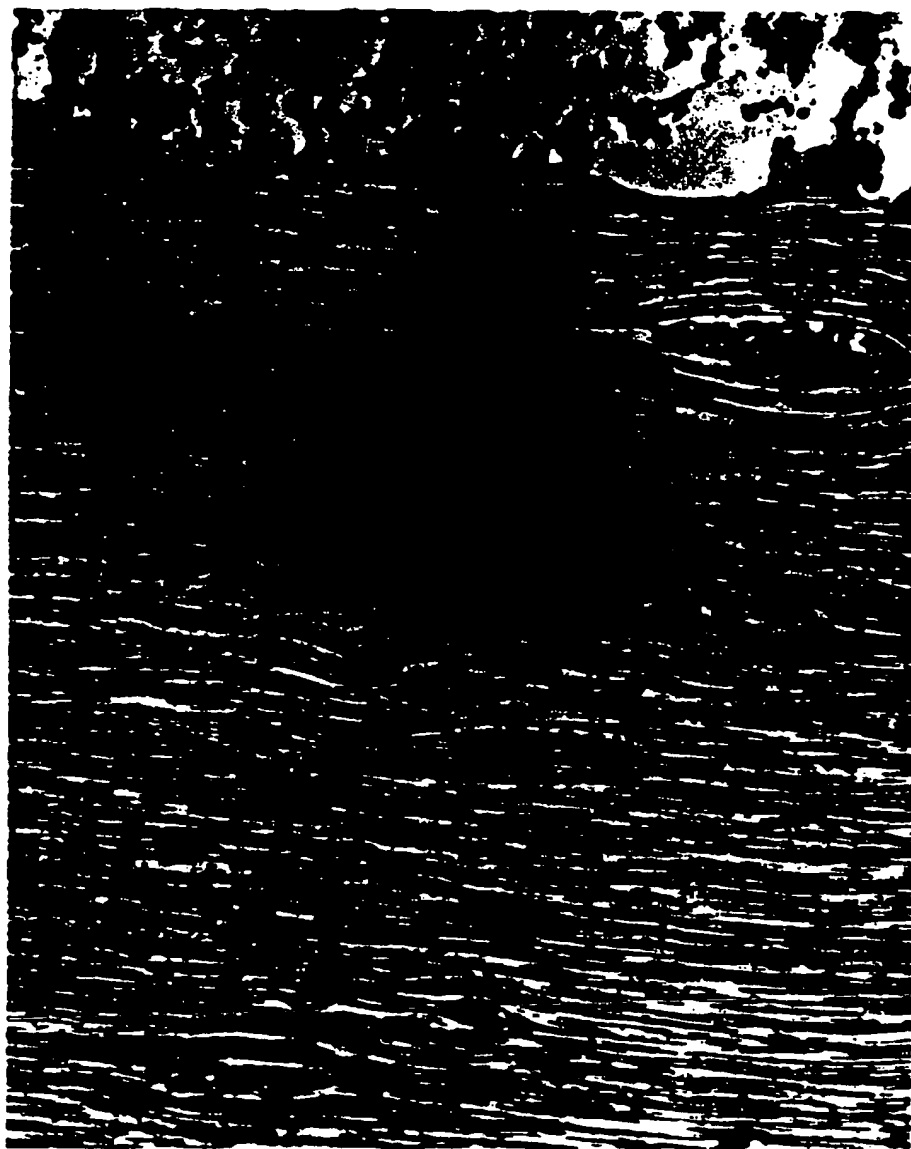
1/5



x10000  $\overline{1\mu}$

FIG. 1

2/5



x10000  $\overline{1\mu}$

FIG.2



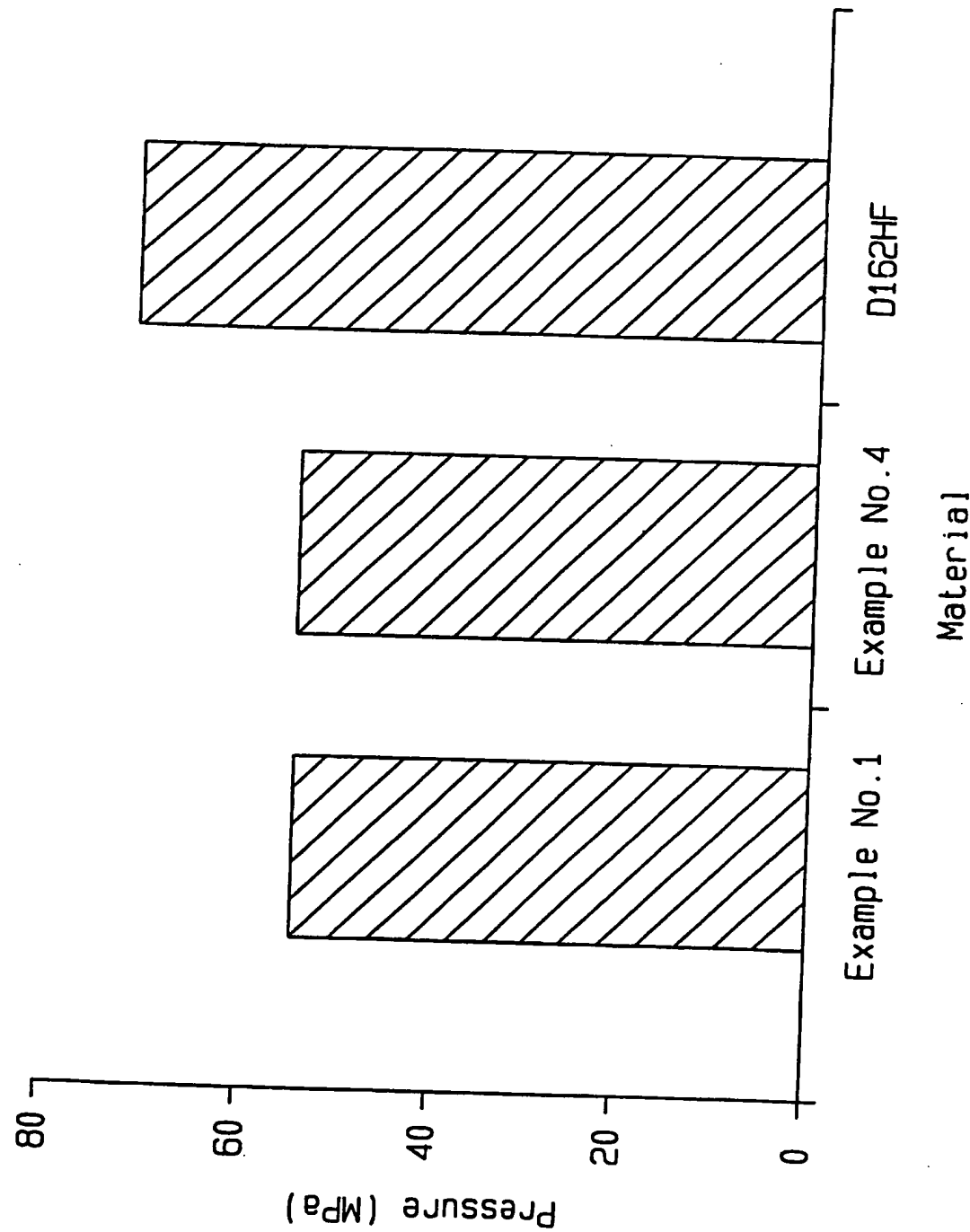
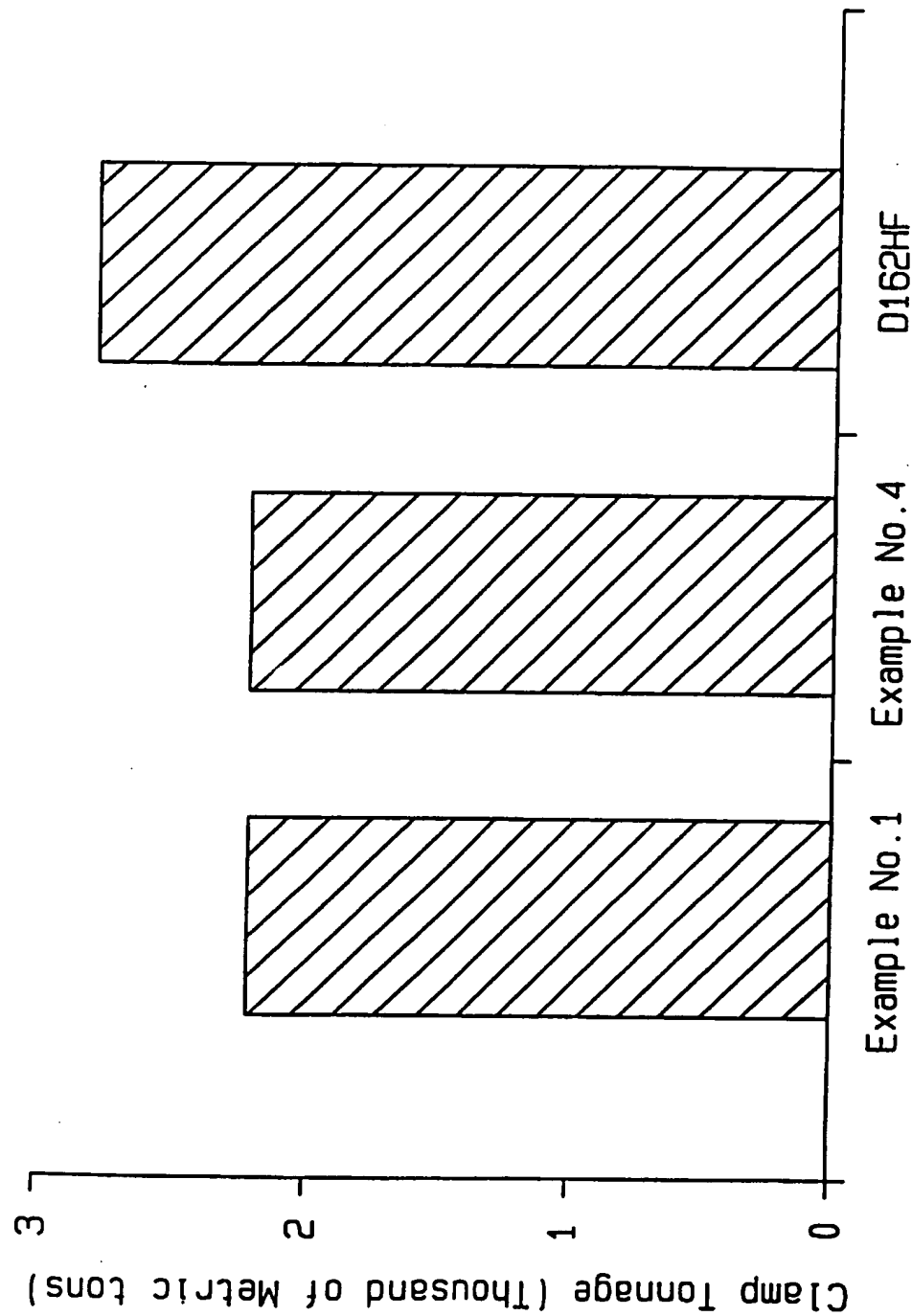


FIG.3

4/5



Material  
FIG.4

5/5

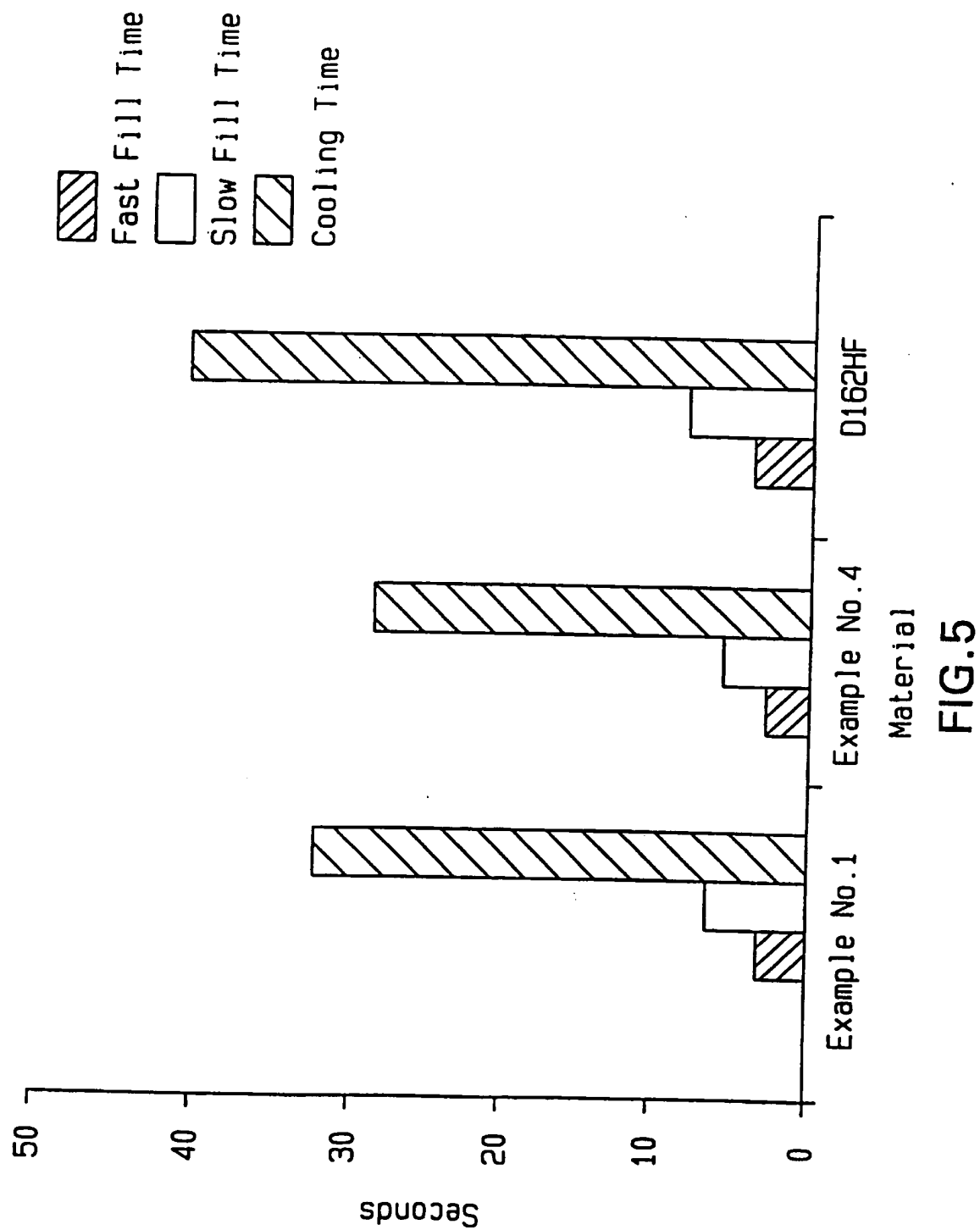


FIG. 5

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/10590

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08L 23/00, 23/04

US CL : 525/240

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/240, 322, 323; 522/112, 157, 158, 161

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US, A, 5,414,027 (DeNICOLA, JR.) 09 May 1995, see entire document.	1-20
Y, P	US, A, 5,416,151 (TANAKA) 16 May 1995, see entire document.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

<p>* Special categories of cited documents:</p>	
*A* document defining the general state of the art which is not considered to be part of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E* earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other means	*Z* document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 OCTOBER 1995

Date of mailing of the international search report

20.11.95

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

*Elizabeth Evans*  
ELIZABETH EVANS

Telephone No. (703) 308-2351

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**